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PREDICTIONS OF NONLINEAR VISCOELASTIC BEHAVIOR USING A HYBRID APPROACH

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Abstract—An approach for nonlinear viscoelastic characterization is presented which uses the combined measurements from creep and dynamic mechanical tests. Although the methodology should extend to several materials and geometries, this research concentrates on thin film polymers used in the manufacture of high altitude scientific balloons. Typically, the constitutive behavior of these materials is characterized through the use of linear viscoelastic techniques. Although this linear approach provides an accurate model for small strains or loads, these materials have been shown to be highly stress dependent and, consequently, it is necessary to identify this nonlinear behavior. Traditional creep measurements require extensive laboratory test times, yet the results obtained from dynamic mechanical analysis provide the capability to predict long term material performance without a lengthy experimentation program. However, dynamic mechanical methods are currently limited to linear response; thus, an approach is presented in which the stress-dependent behavior is derived from short-term creep measurements in a manner analogous to time-temperature superposition. Predictions of material response using linear and nonlinear approaches are compared with experimental results obtained from traditional long-term creep tests. Although linear predictions deteriorate for large stresses, excellent agreement is shown for the nonlinear model. Copyright © 1996 Elsevier Science Ltd

NOMENCLATURE

a_T	temperature-dependent shift factor
a_σ	stress-dependent shift factor
$D(t)$	creep compliance
D_o	elastic component of $D(t)$
D'	storage compliance
D''	loss compliance
E^*	complex modulus
E'	storage modulus, real part of E^*
E''	loss modulus, imaginary part of E^*
g_o, g_1, g_2	nonlinear material parameters
T	temperature
t	time
ΔD	transient component of $D(t)$
$\Delta\varepsilon$	magnitude of oscillatory strain
$\Delta\sigma$	magnitude of oscillatory stress
δ	material damping
ε	strain
ε_t	creep component of strain
σ	stress
σ_o	stress due to preload
τ	relaxation time, dummy variable for time
Ψ	reduced time
ω	frequency

INTRODUCTION

The authors present a method to describe nonlinear viscoelastic behavior of thin film polymer materials. The primary objectives of this research include accurate measurement of viscoelastic properties using dynamic mechanical methods and the development of a nonlinear constitutive model which uses these measurements. Three principles are considered in this research: the superposition of material properties measured at different conditions, such that measurements at one condition (temperature or load) are equivalent to measurements at another condition but on a compressed or expanded time scale; the transformation of measurements obtained in the frequency domain to properties in the time domain, such that characterization is performed on a much shorter time scale; and the characterization of nonlinear behavior in a manner analogous to modeling temperature-dependent behavior, such that superposition principles are used. Measurements obtained from dynamic mechanical tests are used to identify nonlinear behavior and establish linear viscoelastic behavior, and measurements from creep tests establish nonlinear parameters.

Many investigators characterize thin film materials using linear viscoelastic techniques. Wilbeck (1981) has developed a constitutive relationship for thin polyethylene films such as those used in high altitude scientific balloons. Wilbeck predicts the state of stress in the film given strain and temperature histories; however, he shows that the properties of these materials exhibit nonlinear behavior due to the dependence of the behavior on the load history. In several studies, the effect of Schapery (1966, 1969) forms the basis for the characterization of nonlinear behavior of viscoelastic materials. Smart and Williams (1972) compare Schapery's theory to the modified superposition principle in which the creep behavior is separated into time-dependent and stress-dependent components. Predictions using the modified superposition principle are poor; however, Schapery's theory is shown to accurately model the constitutive behavior. In another investigation, Dillard *et al.* (1987) compares Schapery's theory to several nonlinear viscoelastic models including the modified superposition principle. Dillard's findings also suggest that Schapery's theory produces the most accurate results. Additionally, Dillard shows that Schapery's theory is appropriate for complex load histories.

A comparison of experimental creep results and predictions using Schapery's theory is presented by Crook (1991). Crook accurately predicts the strain response of polycarbonate materials to a three-step stress input. In another study, Popelar *et al.* (1990) analyzes a comprehensive set of experimental data obtained from stress relaxation and constant strain-rate tests. Again, the relaxation data are utilized to develop the nonlinear constitutive model, and the nonlinear response is accurately characterized by Schapery's theory. Rand *et al.* (1995) present predictions using traditional creep measurements and Schapery's developments; however, their results are constrained by the time necessary to measure the constitutive properties and the limited ability to isolate the initial components of the viscoelastic response. These studies have shown that Schapery's theory is the most general and the most adaptable of the examined techniques.

Herein, the investigators use a technique to predict nonlinear viscoelastic response based on Schapery's theory and incorporate results derived from dynamic oscillatory tests. Strganac *et al.* (1991, 1995) and Letton *et al.* (1992) have examined materials from NASA's Long Duration Exposure Facility. The linear viscoelastic characteristics of these materials are determined using dynamic mechanical methods. These studies confirm that, although the linear approach provides an accurate approximation for small strains or loads, predictions based upon a linear test and analysis approach deteriorate for moderate to high stress levels. Tests verify that nonlinear viscoelastic response is induced by large stresses and this nonlinear behavior is not appropriately treated in dynamic mechanical testing methodologies. Yet, dynamic mechanical testing is important as transformation of measurements obtained in the frequency domain into properties in the time domain provides viscoelastic characterization on a much shorter time scale. Strganac *et al.* (1995) describe the initial efforts to examine nonlinear behavior of materials using superposition of measurements obtained from dynamic mechanical methods.

ANALYTICAL APPROACH

The nonlinear theory developed by Schapery (1969) is used. If strain is the variable of interest, Schapery shows that the constitutive behavior may be described by

$$\varepsilon(t) = g_o D_o \sigma(t) + g_1 \int_o^t \Delta D(\Psi - \Psi') \frac{\partial g_2 \sigma}{\partial \tau} \mathrm{d}\tau \tag{1}$$

where g_o, g_1, and g_2 are stress-dependent parameters. This equation is a modification of the single integral solution for linear viscoelasticity at a constant temperature and reduces to the well-known Boltzmann superposition integral for linear cases. The term g_o introduces nonlinear contributions in the elastic response due to the level of stress, the term g_1 introduces nonlinear contributions in the complete transient response, and the term g_2 introduces nonlinear contributions due to the rate of the applied load. Ψ and Ψ' are reduced to time variables which are dependent upon the magnitude of the stress, thus

$$\Psi = \Psi(t) = \int_0^t \frac{dt}{a_\sigma} \tag{2}$$

$$\Psi' = \Psi'(\tau) = \int_o^\tau \frac{dt}{a_\sigma} \tag{3}$$

and a_σ is the stress-dependent shift factor.

Schapery (1969) and Rand (1995) describe the approach required to derive the nonlinear parameters from creep and recovery tests. In the effort described herein the authors predict the creep response due to a single step load. For this particular case, eqn (1) is simplified to the following form

$$\varepsilon(t) = g_o D_o \sigma + g_1 g_2 \sigma \int_o^t \Delta D(\Psi)\, dt \tag{4}$$

where D_o and ΔD are developed from measurements associated with linear viscoelastic response, and the terms g_1 and g_2 are combined with a_σ to form a single nonlinear parameter for this particular case. Schapery shows a simplification of eqn (4) if the transient compliance may be represented by a power law of the form $\Delta D = D_1 t^n$. Thus, eqn (4) is rewritten as

$$\varepsilon(t) = g_o D_o \sigma + D_1 \sigma \left(\frac{t}{a_\sigma}\right)^n \tag{5}$$

in which a_σ reflects the effect of $g_1\, g_2$.

Time-temperature correspondence principles (see Ferry (1980)) are used to expeditiously characterize the linear viscoelastic properties which identify ΔD and D_o. Properties measured at one temperature and frequency correspond to the properties at another temperature and frequency through a temperature-dependent shift factor, a_T. The shift factor is determined by the superposition of measurements at two distinct temperatures. Thus,

$$E^\ddagger(\omega, T_1) = E^\ddagger(\omega a_T, T_2) \tag{6}$$

where $E^\ddagger$ represents either the complex modulus (E^*) or a component of the complex modulus (E' or E''). Properties measured at one temperature are equivalent to those at a second temperature on a compressed or expanded frequency scale. The effect of a change in temperature is equivalent to measurements on a different frequency scale. A master curve of the dynamic modulus is formed for a reference temperature and describes the behavior over a broader range of frequencies.

Traditional creep measurements require significant test times to adequately characterize the material response for a long time period. However, the transformation of measurements in the frequency domain to properties in the time domain provides rapid characterization and, as a consequence, long experimentation is eliminated. The method of Ninomiya and Ferry (see Ferry (1980)) is used to transform from measurements obtained with dynamic mechanical tests to the compliance

$$D(t) = D'(\omega)+0.40D''(0.4\omega)-0.014D''(10\omega)|_{\tau=1/\omega} \tag{7}$$

where D' and D'' are complex compliance terms and t is the time derived from $1/\omega$.

Although the authors are developing an approach to derive the separate nonlinear parameters g_1, g_2, and a_σ using dynamic mechanical methodologies, many issues are unresolved with these preliminary efforts (see Strganac *et al.* (1995)). However, for the case of the single step load input as discussed herein, creep tests (performed on a relatively short time scale) may be used to determine the nonlinear shift factor a_σ which also contains the effect of $g_1 g_2$. The nonlinear parameter g_o is determined from dynamic mechanical tests. Using an approach analogous to time-temperature superposition, time-stress superposition is used to identify stress-dependent shift factors. Properties measured at one preload and time correspond to the properties at another preload and time through a preload dependent shift factor, a_σ. The shift factor is determined by the superposition of measurements at two distinct preloads. Thus,

$$D(t, \sigma_{o,1}) = D(t/a_\sigma, \sigma_{o,2}) \tag{8}$$

where D is the compliance measured with the creep test. Properties measured at one preload are equivalent to those at a second preload on a compressed or expanded time scale. The effect of a change in preload is equivalent to measurements on a different time scale. A master curve of the compliance is formed for a reference preload and describes the behavior over a broader range of time. The reference preload is the preload at which nonlinear behavior is first observed. Again, it is noted that for the case described herein the effects of g_1 and g_2 are contained within a_σ; for predictions of cyclic loading, the nonlinear parameters g_1 and g_2 as well as the stress-dependent shift factor a_σ must be individually identified (see Rand *et al.* (1995)).

EXPERIMENTAL METHODOLOGY

Dynamic mechanical tests are used to measure the linear viscoelastic properties (see Ferry (1980)). Measurements are obtained through a sweep of frequencies at a constant temperature and preload. The temperature is changed and new measurements are obtained through a sweep of frequencies. Two parameters are measured—the force due to an oscillatory deformation input and the phase lag. Material damping is derived from the phase lag, δ, between the force (stress) response output,

$$\sigma(t) = \sigma_o+\Delta\sigma\, e^{i(\omega t+\delta)} \tag{9}$$

and the oscillatory deformation (strain) input,

$$\varepsilon(t) = \varepsilon_t+\Delta\varepsilon\, e^{i\omega t} \tag{10}$$

In eqns (9) and (10), σ_o is the stress resulting from the preload which is held constant during the test, $\Delta\sigma$ is the measured stress response, ε_t is the creep strain which occurs during the test, and $\Delta\varepsilon$ is the magnitude of the oscillatory strain input. The complex modulus is derived from these measurements as

$$E^*(\omega, T) = \frac{\Delta\sigma\, e^{i(\omega t+\delta)}}{\Delta\varepsilon\, e^{i\omega t}} = |E|\, e^{i\delta} = |E|\cos\delta+i|E|\sin\delta \tag{11}$$

where $|E|\cos\delta$ is the storage modulus, E', and $|E|\sin\delta$ is the loss modulus, E''. Complex compliance terms D' and D'', as used in eqn (7), are derived directly from E' and E''.

Dynamic mechanical measurements are conducted with the Rheometrics Solids Analyzer (RSA II). Measurements are obtained at 5 frequencies per decade for a sweep of frequencies from 0.4 to 100 rad/sec at a constant temperature. The amplitude of the oscillatory strain is 0.06%. A preload is used to maintain tension on the specimen throughout the test cycle; this preload ranged from 0.69 to 1.03 MPa depending upon the temperature. The temperature is changed at 5°C increments with a 30 second soak prior to the next frequency sweep. Temperatures for the tests range from −150°C to +85°C. The nominal length of each test specimen is 25.4 mm, the nominal width is 6.35 mm, and the nominal film thickness is 0.0203 mm.

Several sources of nonlinear behavior exist in dynamic mechanical tests which will adversely affect measurements of the complex modulus or compliance (see Letton *et al.* (1992) and Strganac *et al.* (1995)). These sources include the magnitude of the oscillatory strain ($|\Delta\varepsilon|$), the value of the preload (σ_o), and the presence of creep (ε_t) which occurs during the oscillatory tests. A preload is used to maintain a tensile load on the specimen throughout the test; however, test results indicate a strong dependence of the measured response at moderate preloads. Herein, the preload is kept to a minimum and the measured properties are verified through calibration tests to be independent of the magnitude of the oscillatory strain and preload. Tests are conducted on a very short time scale and, as a consequence, creep is ignored.

The stress dependent behavior is characterized by separate creep (see Rand (1995)). The experimental data consist of strain measurements obtained for a range of preloads at a constant temperature. The nominal length of each test specimen is 610 mm, the nominal width is 25.4 mm, and the nominal film thickness is 0.0203 mm. Creep is measured over a two-hour period for preloads ranging from 1.5 to 4.5 MPa at 0.5 MPa increments. The test temperature is 23°C. The data establishes a family of stress dependent curves relating the compliance to time; this family of curves is used to form a master curve which provides the compliance over a larger range of time for a reference preload (the preload at which the behavior becomes nonlinear). Stress dependent shift factors are produced as a result of shifting and "superposing" the measured data.

RESULTS

The investigators examine the response of a thin film polyethylene, Stratofilm® (SF-372), which is used in the fabrication of high altitude scientific balloons. Stratofilm® is a linear-low density polyethylene manufactured by Winzen International, Inc. The film is produced through a blown-film extrusion process which induces a directionality in the properties of the material. Results are presented for measurements conducted in the "machine" direction (the direction of the extrusion).

Measurements of the storage compliance are presented in Fig. 1 for temperatures ranging from −50°C to +80°C. Although measurements have been obtained at 5°C increments, temperature increments of 10°C are shown for clarity; and although measurements have been obtained at lower temperatures (less than −50°C), these measurements translate to an extremely short time response which has minimal effect on the results of the present study. However, based on these measurements, the nonlinear parameter g_o which is associated with the elastic component of the compliance is found to be unity for this material.

A master curve of both the storage and loss components of the complex compliance is presented in Fig. 2 for a reference temperature of +20°C. The storage compliance is well-behaved (that is, the data "superposed" easily). Superposition of the loss compliance data is matched to the shifting of the storage compliance. The loss compliance data shows significant scatter, particularly at low frequencies associated with higher temperatures and/or longer times. The effect of the scatter will have minimal impact on the creep compliance since the material response is dominated by the storage compliance (typically one order of magnitude as seen in Fig. 2). Furthermore, the time scale for predictions is on the order of $15 \cdot 10^6$ sec; thus, information on the master curves at frequencies lower than $\approx 10^{-7}$ rad/sec will have little to no effect on predictions of interest. The temperature dependent shift factors associated with the superposition of the data are presented in Fig. 3.

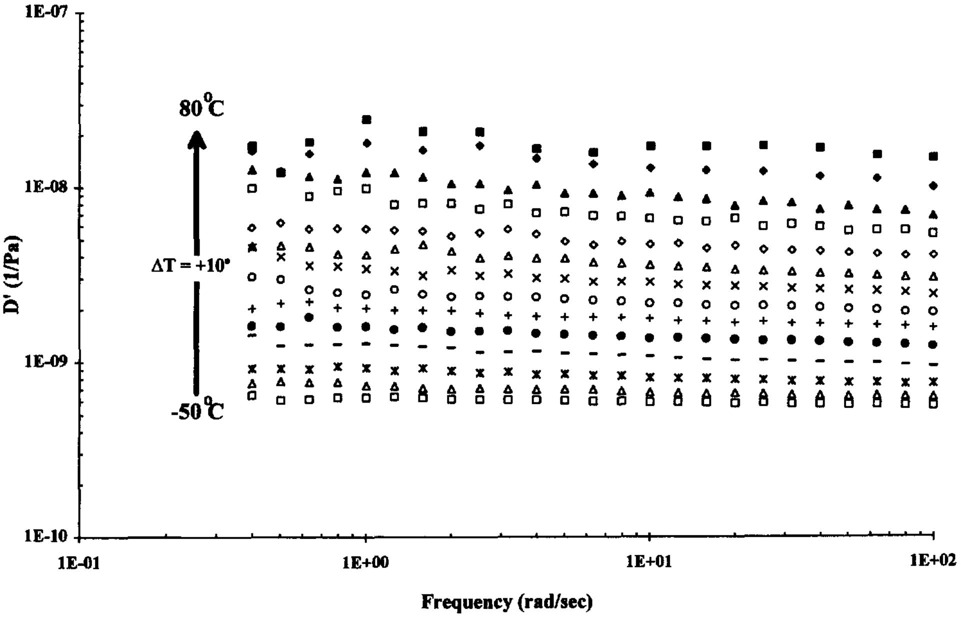

Fig. 1. Components of the complex compliance are derived from dynamic mechanical measurements of the complex modulus. The storage compliance is presented for measurements of Stratofilm® in the machine direction.

The complex compliance data are fit to the curves as shown on Fig. 2 and used to develop the creep compliance, shown in Fig. 4, using the method of Ninomiya and Ferry (see eqn (7)). The creep compliance is developed for a reference temperature of +20°C; however, the compliance translates to other temperatures through the temperature dependent shift factors. For example, the creep compliance curve shifts to the right for the temperature at which the balloon material is typically exposed (roughly −50°C). The

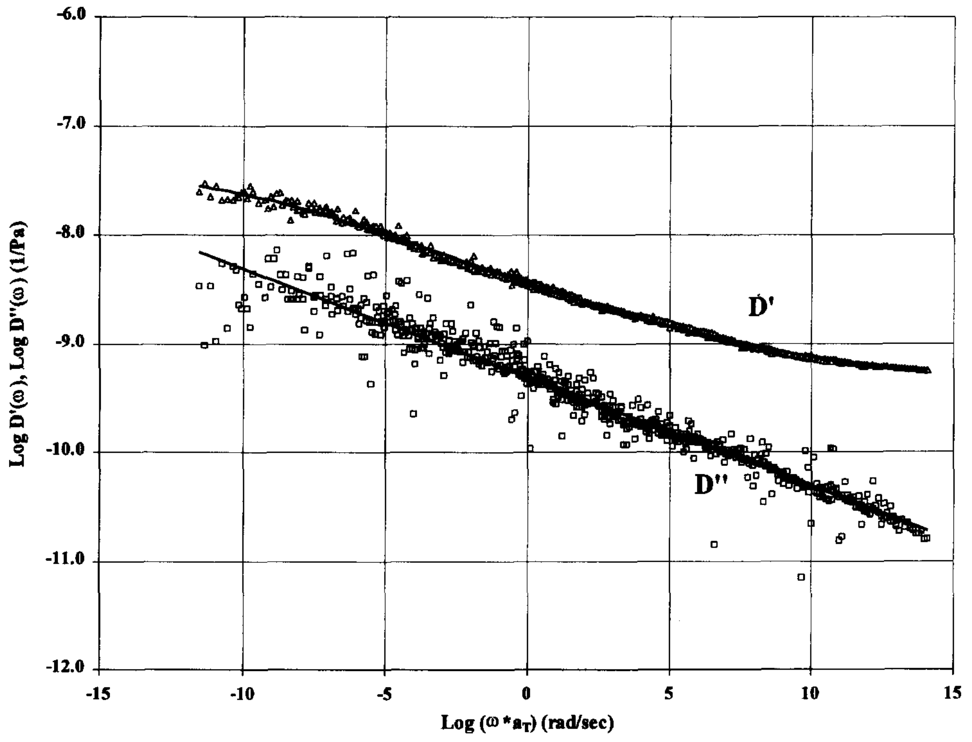

Fig. 2. Master curves of the complex compliance for Stratofilm® (machine direction) are developed from the superposition of measurements obtained at several temperatures ($T_{ref} = 20°C$).

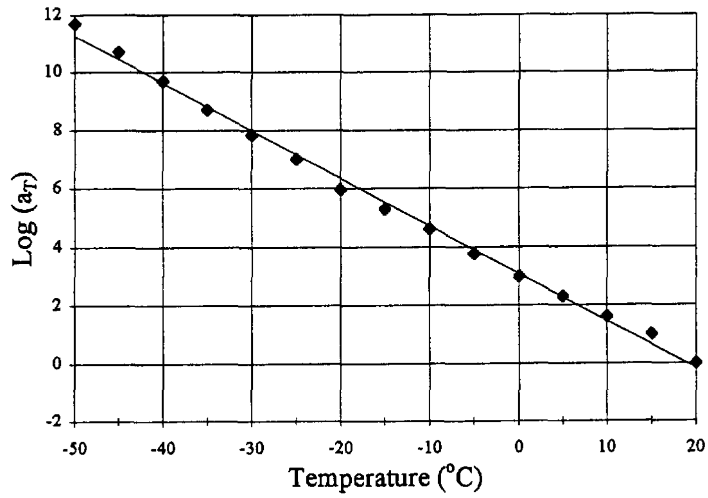

Fig. 3. Temperature dependent shift factors, determined by the superposition of measurements obtained at several temperatures (Fig. 1), are presented for Stratofilm® (machine direction).

compliance is fit to a power law which satisfies the model described by eqn (5). The fit is composed of two parts: the first part is the compliance on the very short time scale which provides D_o and represents behavior at colder temperatures and higher frequencies; the second part is the compliance on a long time scale which provides D_1 and n, and represents behavior at warmer temperatures and lower frequencies.

The complex compliance is dependent upon the preload for predictions of nonlinear creep response. Measurements of creep at several preloads are adequate to provide the stress-dependent shift factors necessary to predict response at constant load and temperature. The creep measurements of Rand *et al.* (1995) as shown in Fig. 5 are used. The data are shifted using time-stress superposition to obtain the master curve in Fig. 6 for a reference preload of 1.5 MPa and reference temperature of 23°C. The stress-dependent shift factors are presented in Fig. 7.

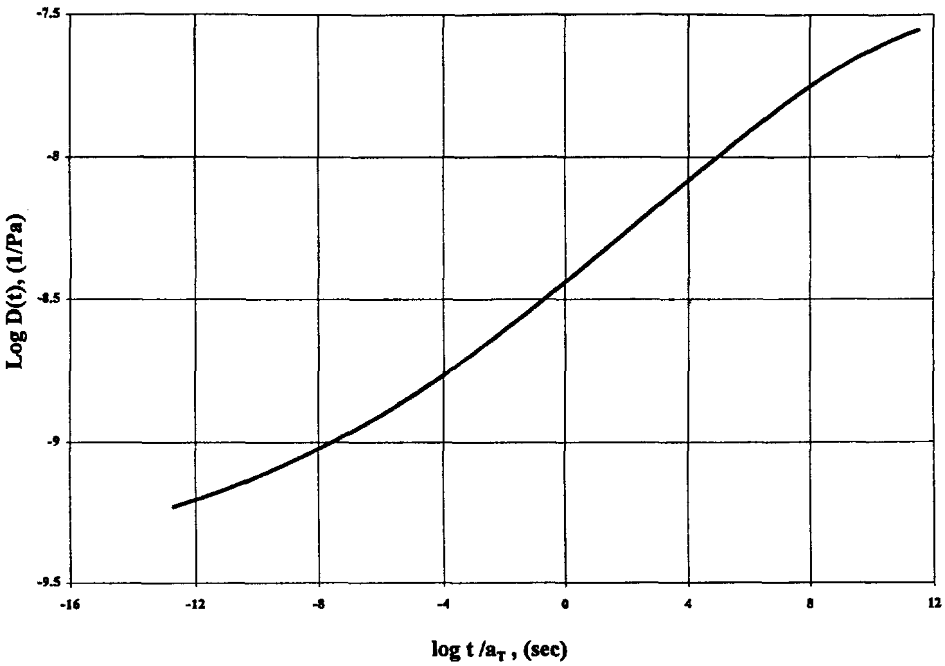

Fig. 4. The creep compliance for Stratofilm® (machine direction, $T_{ref} = 20°C$) is derived from the method of Ninomiya and Ferry. The data satisfies a power law and provides the parameters D_o, D_1, and n for the constitutive model.

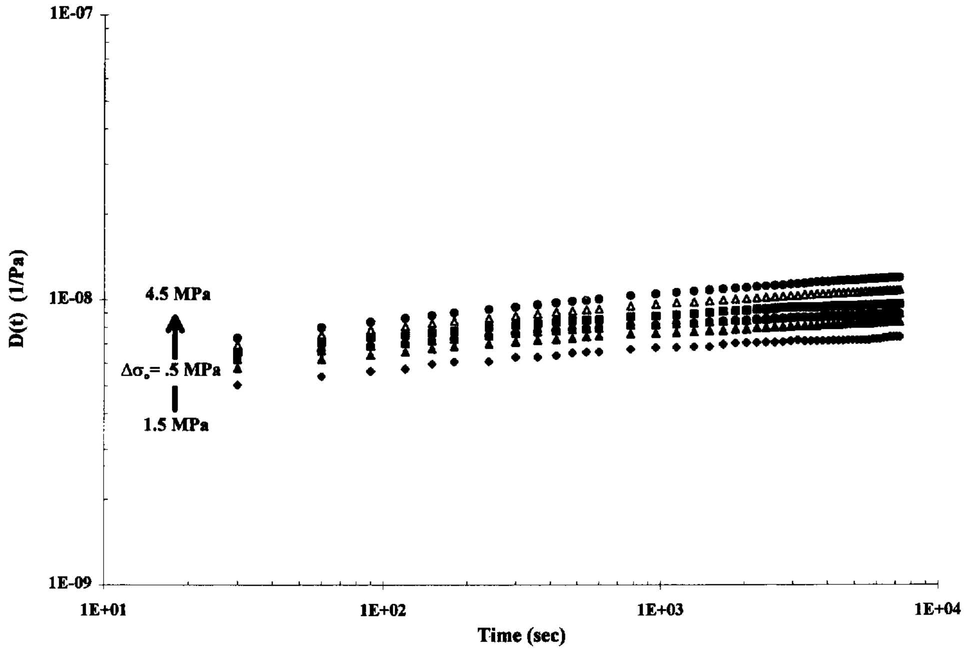

Fig. 5. Creep measurements for Stratofilm® (machine direction, $T_{ref} = 23°C$) are obtained at several preloads (data courtesy of Winzen Engineering, Inc., see Rand (1995)).

Predictions of material response using both the linear and nonlinear approaches are presented in Fig. 8. Linear response is predicted using the creep compliance derived from the dynamic oscillatory measurements. Nonlinear response is predicted using the creep compliance derived from the dynamic oscillatory measurements augmented by the stress dependent shift factors derived from creep tests. These predictions are compared with measurements (see Said (1994)) obtained through traditional creep tests conducted over a six month period. Two stress levels are examined. Predictions which use only linear properties deteriorate at the higher preload.

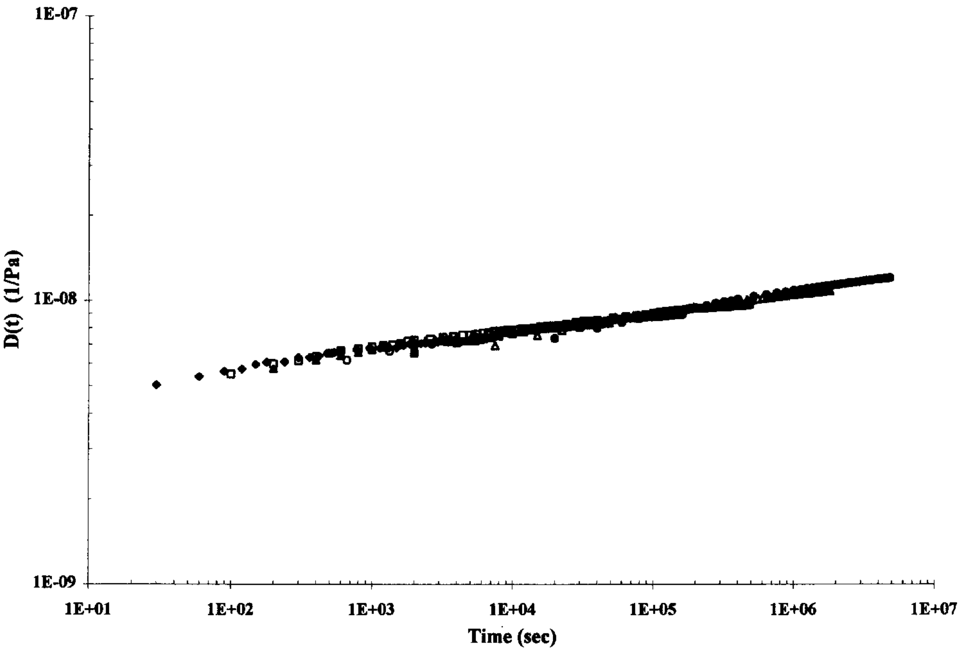

Fig. 6. A master curve of the creep compliance for Stratofilm® (machine direction) is developed from the superposition of measurements obtained at several preloads ($T_{ref} = 23°C$).

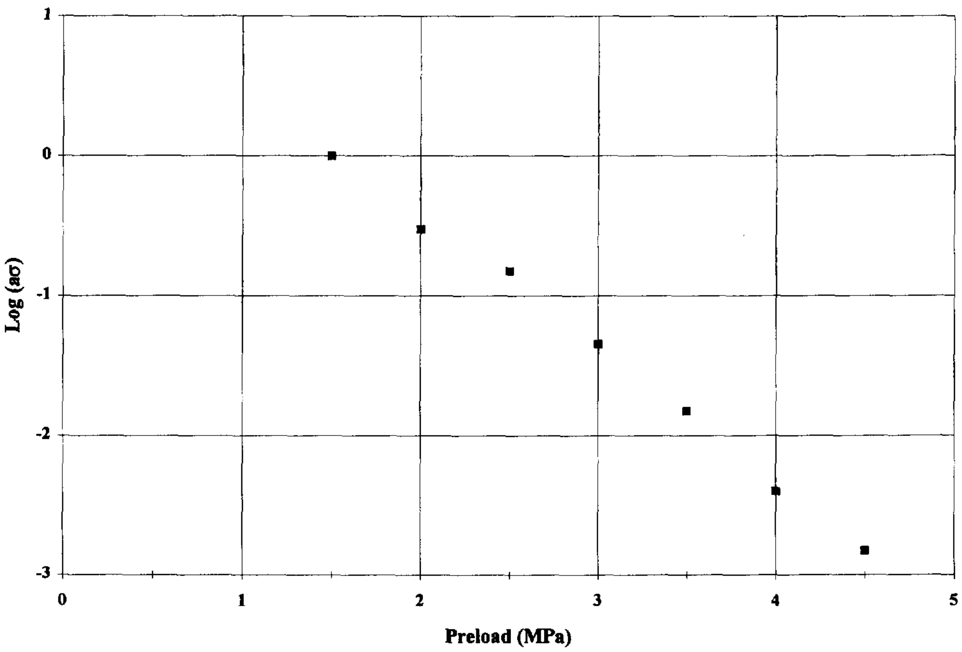

Fig. 7. Stress dependent shift factors, determined by the superposition of measurements obtained at several preloads (Fig. 5), are presented for Stratofilm® (machine direction).

CONCLUDING REMARKS

The authors examine the use and limitations of dynamic mechanical test and analysis methods to quickly characterize the constitutive behavior of thin film polyethylene. These materials are used in the fabrication of high-performance, high altitude scientific balloons. Nonlinear viscoelastic response for materials in service for periods exceeding six months is predicted with a hybrid approach using measurements obtained from both dynamic mechanical and short-term creep tests. Results show that nonlinearities such as stress-dependent

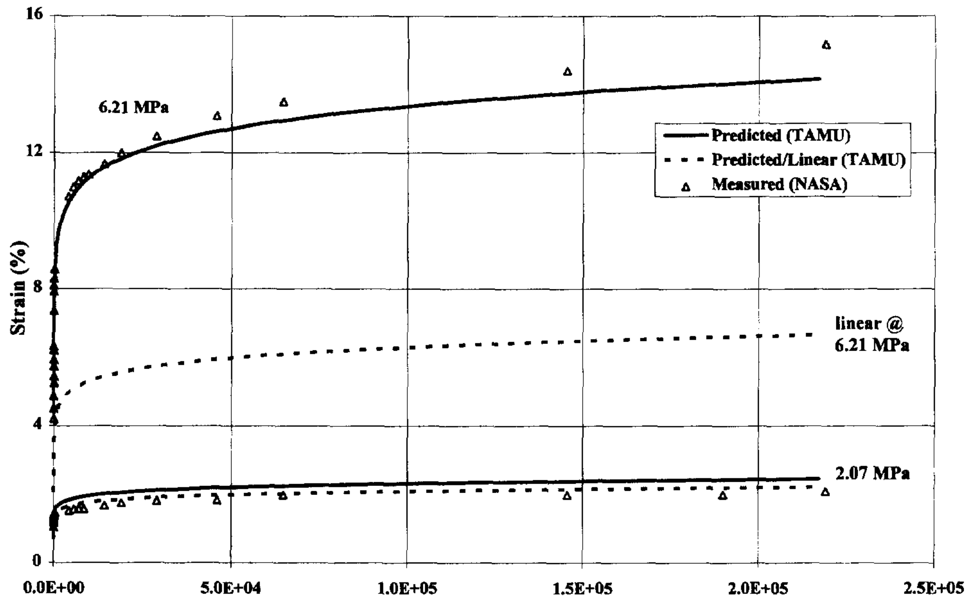

Fig. 8. Nonlinear creep response is predicted for Stratofilm® (machine direction) using the compliance (see Fig. 4) derived from dynamic mechanical tests and the stress dependent parameters (see Fig. 7) derived from creep tests. A comparison is made with traditional creep measurements (data courtesy of NASA-GSFC/WFF, see Said (1994)).

contributions must be included in the characterization of materials exposed to higher stresses. Unfortunately, dynamic mechanical test and analysis methods are sensitive to several sources of nonlinearities which include preload, oscillatory input, and underlying creep strain. With identification and avoidance of these nonlinearities, dynamic mechanical tests and time-temperature correspondence principles are used to develop the linear properties of the material, and the effective transformation of measurements obtained in the frequency domain to material behavior in the time domain allows for linear characterization of the constitutive behavior with a short test program. Predictions of material response are consistent with the results of traditional creep tests at low stress levels but these results underscore the need to examine stress-dependent behavior as predictions clearly deteriorate for larger stresses. Consequently, these predictions require an identification of the nonlinear behavior; for the case presented herein, the nonlinear parameters are identified by creep tests performed for a period of time (two hours) which is significantly less than the time of the predicted response (six months). Predictions of the nonlinear response have excellent agreement with experimental measurements for the materials examined. Furthermore, it is noted that the creep tests for the comparisons in this study require a test time in excess of six months, yet the predictions for the case presented herein use properties derived from roughly a single day of tests.

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